REDUCING ACTION OF METALLIC CALCIUM AND CALCIUM HYDRIDE UPON METALLIC OXIDES, SULPHIDES, AND HALOGEN SALTS.

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(*A Paper read before the Faraday Society, Tuesday, October 29, 1907,* Mr. N. T. M. Wilsmore, M.Sc., *in the Chair.*)

In a previous paper read before this Society (this vol., p. 115) one of us has shown that metallic calcium is a particularly energetic reducing agent when mixed with metallic oxides or sulphides, the reaction being started either by heating in the furnace or by means of a fuse consisting of a mixture of calcium and barium or sodium peroxide. This work has been continued, and we have also tried the action of calcium hydride as a reducing agent in place of the metallic calcium. Although calcium hydride may be used successfully in certain cases, it is not so energetic a reducing agent as metallic calcium itself. This, of course, is to be expected, because the formation of calcium hydride by the action of hydrogen upon molten calcium is an "exothermic" reaction, considerable heat being evolved. In fact, if hydrogen gas is passed sufficiently rapidly into molten calcium, the reaction once commenced will continue without further addition of heat until the whole of the metal has been converted into the hydride (German Patent 188,570). Consequently, when calcium hydride is mixed with a metallic oxide and the mixture heated, before reaction can take place a certain amount of heat is required to decompose the hydride. Now, although in many cases the reaction once started will go on—and is therefore exothermic—until the whole of the oxide is reduced, the temperature of reaction can never be so high as when metallic calcium alone is employed, because a portion of the heat of reaction will be required to decompose the hydride as the reaction proceeds. Beside trying calcium hydride as a reducing agent, further experiments have been carried out with metallic calcium. We find in the latter case that tungstic oxide is readily reduced, and the tungsten can be obtained as a molten mass. With titanic oxide the reaction is less vigorous and the heat is not sufficient to melt the metal produced.

We have also found that the hydroxides of the alkali metals are readily reduced by means of calcium, and also barium and strontium hydroxides. The heats of formation of the hydroxides are as follows—

Ca, O, H_2O	...	...	...	...	...	160,540 cals.
Sr, O, H_2O...	...	...	...	...	...	146,140 „
Ba, O, H_2O	...	...	...	...	...	———
Na_2, O, H_2O	...	...	...	...	...	135,380 „
K_2, O, H_2O...	...	...	...	...	...	137,980 „

Consequently, the reactions with metallic calcium should be exothermic, and once they are started should go on to conclusion. In carrying out these reactions the metallic calcium, in the form of turnings, was placed on the

bottom of an iron crucible and covered with the broken alkali hydroxide; the reason for proceeding in this manner was because of the difficulty experienced in powdering the deliquescent hydroxide. The flame of a blowpipe was then played against the upper part of the crucible in order to melt the hydroxide and to cause it to run down upon the calcium. The reaction once started in this manner then went on until the whole of the material had been reacted upon. In the case of sodium, lithium, potassium, rubidium, and cæsium the metals were vapourised and burnt round the edge of the crucible lid. With strontium and barium hydroxide the substances were ground up and intimately mixed with the metallic calcium.

Of course, too much reliance cannot be placed upon the reactions between the hydroxides. The temperature of the reaction is, for example, certain to be lowered by the amount of heat required to vapourise the water, because finally not $Ca(OH)_2$ but CaO is produced. The reactions, however, are exothermic, because when anhydrous strontium or barium hydroxides are mixed with an equivalent of metallic calcium—

$$Sr(OH)_2 + Ca = Sr + CaO + H_2O,$$

the mixture is readily fired by means of a fuse, and the reaction once started goes on until the whole of the mixture has reacted. Strange to say, however, we have not managed to obtain a metallic regulus from the hydroxides; the explanation of this is given later.

The heats of formation of the oxides are as follows (we have taken the numbers given by Professor J. W. Richards, *Electrochemical and Metallurgical Industry*, **6**, 8, except for calcium, where we have employed the value given by Moissan by actual measurement)—

Ca, O	**145,000***
Mg, O	143,400
$\frac{1}{3}Al_2, O_3$	130,870
Sr, O	128,440
Na_2, O	100,900
Ba, O †	104,000?
$\frac{1}{2}Si, O_2$	98,000
Zn, O	84,000
$\frac{1}{2}Sn, O_2$	70,650
$\frac{1}{3}Fe_2, O_3$	65,200
Pb, O	50,800
Sulphides.	
Ca, S	**94,300**
Mn, S	45,600
Na_2, S	89,300
Zn, S	43,000
Pb, S	20,200

With the sulphides calcium reacts vigorously; the heats of formation given above show that this should be the case. But there is a tendency for the calcium to react with the sulphide to form a thio-compound, such as $Ca_3(SbS_3)_2$; although we have not analysed the slag produced, this seems the most probable explanation of the small amount of metal produced in these reactions. On the other hand, it may be that sub-sulphides are produced

see p. 184).

* Richards 131,500.

† The number for BaO is certainly too low; in the determinations the barium used was always obtained from the amalgam and contained traces of mercury.

Experiments were also tried with the chlorides, the heats of formation of which are as follows—

Ca, Cl_2	... ...	**183,890** cals.
Sr, Cl_2	... ...	184,560 „
Ba, Cl_2	... ...	———
K_2, Cl_2	... ...	211,220 „
Na_2, Cl_2	... ...	195,380 „
Li_2, Cl_2	... ...	187,620 „
$\frac{1}{3} \cdot Al_2, Cl_6$	... ...	107,320 „
Pb, Cl_2	... ...	82,770 „

From the heats of formation it follows that the reactions between metallic calcium and potassium, strontium, sodium, and lithium are endothermic, and therefore for the reactions to take place completely it will be necessary to add heat from an external source. As a matter of fact, these reactions cannot be started by means of a fuse. But they can be made to take place by playing the blow-pipe flame on to an iron crucible in which the mixtures are contained. Another method by which the reaction can be caused to take place is to mix a certain quantity of iron oxide and calcium with the alkali chloride and calcium, thus—

$$Fe_2O_3 + 3\,Ca = 2\,Fe + 3\,CaO + 240{,}000 \text{ cals.}$$

The great amount of heat generated by this reaction is sufficient to cause the reaction—

$$Ca + 2\,NaCl = CaCl_2 + 2\,Na - 11{,}490 \text{ cals.}$$

to go on to completion. On the other hand, the reactions between aluminium chloride and calcium and lead chloride are exothermic and take place with great readiness. In fact, it is difficult to control them, a large portion of the contents of the crucible frequently being ejected.

It has not been found possible to obtain pure strontium or pure barium by reacting with metallic calcium and the respective chlorides, the metal regulus produced being always contaminated with more or less calcium. When the theoretical proportions of the materials are mixed and reaction caused to take place by the addition of an external source of heat very little metal is obtained, probably owing to the formation of a sub-chloride, thus—

$$BaCl_2 + Ca = ClBa\text{-}CaCl.$$

But when two atoms of calcium are employed the reaction is very much more vigorous, and a metallic regulus is obtained ; it is, however, an alloy of calcium and barium or calcium and strontium, as the case may be. Theoretically one might expect to obtain the sub-chloride—

$$BaCl_2 + 2\,Ca = Ba + Ca_2Cl_2,$$

but only a portion of the calcium reacts with the $CaCl_2$ first produced, the remainder alloying with the alkaline metal as it is formed.

Experimental.

(*Calcium Hydride.*)

Copper Oxide.—When molecular proportions of copper oxide and calcium hydride, according to the following equation, are intimately mixed together—

$$2\,CuO + CaH_2 = 2\,Cu + CaO + H_2O,$$

and fired by a fuse, or even by means of a taper, a very vigorous reaction ensues and volumes of steam are given off, showing that both the calcium and the hydrogen enter into the reaction. The cooled product, which was black on the surface, owing to superficial oxidation, was treated with dilute hydrochloric acid, until on filtering and washing a test for calcium was no longer given. It was then washed with water and alcohol and dried in the steam oven. The copper so obtained was in the form of a fine powder, only a portion of it having been fused into small metallic globules. It is evident, therefore, that the heat of reaction is only a little above the melting-point of copper. The temperature would not, therefore, rise much above 1,100°, at any rate on a small scale.

Manganese Peroxide (Pyrolusite).—In this case it was not found possible to start the reaction by means of a fuse. The crucible was therefore placed in a crucible furnace and strongly heated. After about five minutes volumes of black smoke and steam came from the furnace, showing that reaction was taking place, probably according to the formula—

$$MnO_2 + CaH_2 = Mn + CaO + H_2O.$$

As the heat of reaction was not sufficient to cause the manganese to fuse, it was obtained in the form of a powder intimately mixed with calcium oxide, therefore it was not attempted to separate them.

Ferric Oxide (Hæmatite).—The crucible containing the mixture was placed in the crucible furnace and heated to bright redness for about an hour. At the end of the time the product was cooled and the dark mass powdered. The iron had not fused, but particles were attracted by a magnet, showing that reaction had taken place.

Lead Monoxide (Litharge).—The mixture was heated to bright redness in the furnace, and on cooling a regulus of molten lead was found at the bottom of the crucible. This experiment was repeated several times, and it was found that the lead did not always run together, but remained as globules interspersed through the calcium oxide. But by stirring with an iron rod the bulk of the lead could be caused to run together at the bottom of the crucible.

Stannic Oxide.—Reaction in this case is very slow, and it was necessary to heat to bright redness. On cooling the mass had a dark grey colour, but no specks of tin were noticed. The experiment was repeated, heating for a longer time—about two hours—to a bright red heat, and towards the end of the operation stirring with an iron rod. On cooling it was found that the tin had partially run together, but a good deal of it still remained mixed with the calcium oxide.

Zinc Oxide.—It was not possible to fire a mixture of calcium hydride and zinc oxide. The mixture was therefore placed in the furnace and heated to bright redness for about an hour. On cooling and examining the mixture it was found that no reaction had taken place.

Tungstic Oxide.—Reaction takes place, but the temperature is not sufficiently high to melt the tungsten produced.

Boron trioxide, when mixed with the equivalent of calcium hydride and strongly heated for two or three hours in a crucible furnace, is reduced. A brownish mass is obtained, and if this is ground up in water and repeatedly boiled with hydrochloric acid until the washings are practically free from calcium chloride, the boron is obtained as a light brown amorphous powder. We have, however, never succeeded in obtaining it free from calcium. Ignited borax is also reduced by means of calcium hydride.

Silica.—Very finely divided silica can be reduced by heating it strongly in the furnace for some hours with calcium hydride. But on treating the mass so obtained with hydrochloric acid, inflammable gas is given off. The reaction in this respect is similar to that which is produced on reducing silica with metallic calcium (this vol., p. 116).

Lead Sulphide.—The mixture could not be ignited by means of a fuse, but upon strongly heating in the furnace reaction took place. Only a small portion of the lead ran down to the bottom of the crucible, the bulk of it remaining interspersed throughout the reactive mixture or combined with the calcium sulphide—

$$2PbS + CaH_2 = 2Pb + H_2S + CaS.$$

Antimony Sulphide.—This mixture is exceedingly readily ignited, it being sometimes possible to cause the action to commence by bringing a lighted taper in contact with it. As the reaction proceeds the mixture in the crucible swells up in an extraordinary manner, reminding one of the peculiar way in which mercury thiocyanate (Pharaoh's serpents) behaves upon being ignited. The hydrogen sulphide evolved takes fire. Very little metal is actually obtained, although the reaction should, one would think, proceed as follows—

$$3Sb_2S_3 + 6CaH_2 = 6CaS + 3H_2S + 6Sb.$$

In all probability, however, to a certain extent a compound of antimony and calcium sulphide is produced, for example, $Ca_3(SbS_3)_2$. Products of a similar nature are also probably formed in the case of lead sulphide. The formation of such compounds would account for the small yield of metal in both cases (*cf.* p. 184).

Metallic Calcium.

As the reactions between tungstic oxide and titanium oxide were not satisfactory, we tried the action of metallic calcium with these two oxides, and the results were much more satisfactory.

Tungsten Oxide.—Metallic calcium and tungsten oxide were intimately mixed together in quantities corresponding to the following equation—

$$WO_3 + 3Ca = 3CaO + W.$$

The mixture was fired by means of a fuse, and an extremely vigorous reaction ensued, an intense white heat being produced. On cooling, the product was removed from the crucible, and at the bottom a reguline ingot of metal was obtained which upon weighing was found almost to correspond to the theoretical amount of metal obtainable. It was extremely hard, and could hardly be marked with a file. In this case the heat of reaction was so extremely high that the calcium oxide was actually fused. This is the only case which we have met with in which the calcium oxide has been completely melted. On the other hand, when mixtures of calcium and aluminium have been used as reducing agents, the mixed oxides have at times been obtained as a fairly readily fusible slag (this vol., p. 117).*

Titanium Oxide.—The reaction in this case is much more vigorous than when the hydride is employed, but even in this case the temperature of the reaction did not rise sufficiently high to fuse the metal.

Aluminium Oxide.—The heat of formation of this oxide Al_2O_3 is 380,000

* Goldschmidt has patented the use of a mixture of calcium and aluminium (American Patent 875,345, December 31, 1907). The best results, he finds, are obtained by using the calcium and aluminium in the proportions necessary to form a calcium-aluminium slag of the composition $3CaO_2,Al_2O_3$, this slag readily fusing to a thin liquid.

cals. In order that this may correspond to CaO, which has a heat formation of 145,000 cals., the number for aluminium oxide should be divided by three, when we obtain 126,666 cals.; therefore metallic calcium should theoretically be able to reduce alumina. As a matter of fact, when aluminium oxide and metallic calcium are mixed together according to the following equation—

$$Al_2O_3 + 3Ca = 3CaO + 2Al,$$

and the mixture fired by means of a fuse, reaction proceeds throughout the mass without further addition of external heat. The reaction, however, is by no means vigorous, and globules of metallic aluminium were not obtained.

Strontium Oxide.—A mixture of molecular proportions of strontium oxide and metallic calcium—

$$SrO + Ca = CaO + Sr,$$

is readily fired by means of a fuse, and the action completes itself without the addition of external heat. The same remark applies to a mixture of barium oxide and calcium. Although in both cases the reaction was very vigorous, no metal was produced. This at first sight seemed difficult of explanation, unless indeed the heat of reaction was sufficient to volatilise the metals produced. It occurred to us, however, that possibly a *sub-oxide* might be produced. We therefore took equimolecular proportions of metallic calcium and of calcium oxide according to the following equation, the oxide having been heated to redness in the furnace to decompose any hydroxide—

$$CaO + Ca = Ca_2O.$$

This mixture was placed in a crucible and covered with asbestos to prevent the egress of air, and then heated in the furnace to bright redness for two hours. On cooling and emptying out the contents of the crucible it was found that the whole of the calcium had disappeared. Portions of the mixture were then treated with water and with hydrochloric acid, but there was no effervescence in either case. It appears, therefore, that a lower oxide of calcium had been produced. We are examining further into the matter. If a lower oxide is produced, then it explains why no metal was obtained with strontium and barium oxides. Sub-sulphides may perhaps also be formed.

Sodium Hydroxide.—The reaction was one of considerable violence, the metallic sodium produced being volatilised and burning at the edges of the lid of the crucible.

The other alkali metals behaved in a similar manner.

In the case of barium and strontium hydroxide the reaction was also very vigorous, but it was never found possible to obtain the metals in the fused condition. The reaction with rubidium hydroxide was particularly vigorous.

Barium Chloride.—On mixing in an iron crucible equi-molecular proportions of anhydrous barium chloride and calcium and heating the crucible by means of the blow-pipe flame, as soon as the crucible gets well heated a vigorous reaction takes place, but the yield of metal is very small. This, as has already been stated, is probably due to the formation of a sub-chloride of barium and calcium. But if two atoms of calcium are used for every molecule of barium chloride taken, then the reaction is excessively vigorous, and a large quantity of a metallic regulus is obtained at the bottom of the crucible, which is an alloy of barium and strontium.

Strontium Chloride.—The reaction in this case is rather more vigorous than with barium. When two atoms of calcium are employed, a large metallic regulus is obtained, but it contains considerable quantities of calcium.

The chlorides of alkali metals—lithium, sodium, potassium, rubidium, and cæsium—all react with calcium in a similar manner to the metals of the alkaline earths. But owing to the volatility of these metals, they were always vapourised, and the metals burnt round the edge of the crucible lid.

Lead Chloride.—Using a mixture of calcium and lead chloride according to the equation—

$$PbCl_2 + Ca = Pb + CaCl_2,$$

and starting the reaction by means of a fuse, a very vigorous reaction took place, a portion of the mixture being thrown out from the crucible. A piece of lead was obtained on removing the reaction mixture from the crucible. It was, however, crystalline and brittle, and consisted of an alloy of calcium and lead.

Aluminium Chloride.—Molecular proportions of calcium and aluminium chloride were placed in a crucible and fired by means of a fuse. The reaction was extremely intense. Aluminium, or an alloy of aluminium and calcium, was obtained on cooling. The yield of metal, however, was small, which would point to the formation of a mixed chloride of calcium and aluminium.

Action of Calcium and Calcium Hydride upon Sulphur, Phosphorus, and Selenium.

When sulphur and metallic calcium are mixed together according to the equation—

$$Ca + S = CaS,$$

and fired by means of a taper, the reaction is so violent that the whole of the product is ejected from the crucible. The reaction with red phosphorus and with selenium is also extremely vigorous.

When calcium hydride is mixed with sulphur in the proportions represented by the equation—

$$CaH_2 + 2\,S = CaS + H_2S,$$

and ignited by means of a fuse, the reaction is vigorous but well under control, a friable mass of calcium sulphide being produced. The calcium sulphide so produced does not show the phenomenon of phosphorescence. Red phosphorus and calcium hydride, when mixed in the proportions represented by the equation—

$$3\,CaH_2 + 3\,P = CaP_2 + PH_3,$$

cannot be ignited by means of a fuse. A satisfactory reaction can, however, be caused to take place by taking a mixture of calcium and red phosphorus according to the equation—

$$3\,Ca + 2\,P = Ca_3P_2,$$

and employing a mixture obtained by combining the two equations. Extremely active rusty red calcium phosphide is obtained in this manner.

Calcium selenide can be produced by mixing molecular proportions of calcium hydride and selenium and igniting by means of a fuse.

Since this paper was read our attention has been drawn to the paper by W. Muthmann and L. Weiss (*Liebig's Annalen*, **355**, 137). In this paper they show, as we have done, that the chlorides of sodium, potassium, barium, and strontium can be reduced by heating with metallic calcium. They have also found that alloys of calcium and barium and calcium and strontium are produced and not the pure metals.